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A.G. Norman, J.M. Olson, J.F. Geisz,
H.R. Moutinho, A. Mason, and M.M. Al-Jassim
National Renewable Energy Laboratory

S.M. Vernon
Spire Corporation

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1617 Cole Boulevard
Golden, Colorado 80401-3393

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Phase separation and facet formation during the growth of $(GaAs)_{1-x}(Ge_2)_x$ alloy layers by metal organic vapour phase epitaxy

A G Norman, J M Olson, J F Geisz, H R Moutinho, A Mason, M M Al-Jassim and S M Vernon[1]

National Renewable Energy Laboratory, 1617 Cole Boulevard, Golden, CO 80401, USA
[1]Spire Corporation, One Patriots Park, Bedford MA 01730, USA

ABSTRACT: Metal organic vapour phase epitaxy $(GaAs)_{1-x}(Ge_2)_x$ alloy layers, $0<x<0.22$, were grown at temperatures between 640° and 690°C, on vicinal (001) GaAs substrates. Phase separation occurred in all the layers. The phase-separated microstructure changed with alloy composition, growth temperature, and substrate orientation. In $x \approx 0.1$ layers grown at 640°C, Ge segregation occurred on {115}B planes associated with a {115}B surface faceting. Increase in growth temperature led to the formation of large, (001)-oriented, irregular-shaped platelets of Ge-rich material. Growth on {115}B substrates resulted in a "natural superlattice" of GaAs/Ge along the growth direction.

1. INTRODUCTION

Two-junction $Ga_{0.52}In_{0.48}P$/GaAs solar cells have demonstrated record-breaking efficiencies (Bertness et al 1994, Takamoto et al 1997). They are in production for space photovoltaic applications and are also leading candidates for concentrator cells in terrestrial applications. More efficient solar cells may be achieved by adding extra junctions in layers with lower band gaps. An ideal material for such an extra junction would be lattice matched to GaAs and have a 1 eV band gap (Kurtz et al 1997). Possible materials fulfilling these requirements are $(GaAs)_{1-x}(Ge_2)_x$ metastable alloys, the subject of this work, and GaInAsN alloys (Friedman et al 1998). GaAs and Ge, despite being size matched, are mutually insoluble in the equilibrium bulk solid state resulting in almost complete phase separation into GaAs-rich and Ge-rich regions at all temperatures below the melting point (Takeda et al 1965, Osório et al 1991). The reason for this phase separation is the high energy required to form Ga-Ge and As-Ge bonds, which do not satisfy the octet rule for valence electrons, observed in the pure components, and the even higher energies predicted for As-As and Ga-Ga antisite bonds (Osório et al 1991). Despite the strong tendency of this alloy toward phase separation, there have been several reports of the growth of relatively homogeneous epitaxial layers of metastable $(GaAs)_{1-x}(Ge_2)_x$ alloys across the composition range using non-equilibrium techniques such as metal organic vapour phase epitaxy (MOVPE), ion-assisted sputter deposition, and molecular beam epitaxy (MBE). Growth of single-phase, metastable alloys was reported by MOVPE in the temperature range 700°–750°C (Alferov et al 1982) and by sputter deposition in the temperature range 450°–550°C (Barnett et al 1982, Romano et al 1987). GaAs-rich sputter-deposited layers, however, contained a network of Ge-mediated antiphase boundaries that percolated between zinc-blende phase/antiphase domains without causing significant antisite formation (Romano et al 1987). Banerjee et al (1984, 1985) reported phase separation in MBE $(GaAs)_{1-x}(Ge_2)_x$ layers grown between 550° and 620°C on (001), (110) and (211) GaAs substrates, resulting in the formation of 10–30 nm, {110}-oriented Ge-rich regions in the surrounding GaAs-rich material. Growths at 430°C on (001) substrates appeared to be single phase. Baird et al (1991) did not find any evidence of phase separation in MBE $(GaAs)_{1-x}(Ge_2)_x$ layers grown on (001) GaAs substrates at temperatures up to 580°C. This system has also attracted considerable theoretical interest (e.g., Osório et al 1991). This is because a transition from the GaAs, zinc-blende structure to the Ge diamond cubic structure has been reported to occur in single-phase metastable alloys at some critical composition x (due to the different crystal structures of the two end-point constituents). In this work we report evidence of phase separation in MOVPE-grown $(GaAs)_{1-x}(Ge_2)_x$ layers (see also Norman et al 1999). The observed segregation exhibits a microstructure completely different from that reported before (to the best of our knowledge) in $(GaAs)_{1-x}(Ge_2)_x$ layers. The phase-

separated microstructure depends on alloy composition, growth temperature, and substrate orientation and, in some cases, is associated with a surface faceting that occurs during growth.

2. EXPERIMENTAL DETAILS

$(GaAs)_{1-x}(Ge_2)_x$ layers, $0<x<0.22$, were grown by low-pressure (≈ 50–70 Torr) MOVPE in two different reactors, at growth temperatures between 640–690˚C, on vicinal (001) GaAs substrates. The source chemicals used for growth were trimethylgallium, arsine, and germane. Substrate rotation was used in one reactor but not in the other. The average Ge content of the layers was measured from a 20 μm diameter area using wavelength-dispersive electron-probe X-ray microanalysis at 10 kV, using La lines and GaAs and Ge as standards, and to an accuracy of ≈0.5 at. %. Transmission electron microscopy (TEM) cross-section samples were prepared by conventional mechanical and ion-milling techniques and examined in a Philips CM30. (110) and $(\bar{1}10)$ cross sections were distinguished using convergent-beam electron diffraction (Taftø and Spence 1982). Atomic Force Microscopy (AFM) was performed in air on the growth surface topography using a Park Scientific Instruments Autoprobe LS in the noncontact mode.

3. RESULTS

Fig. 1 shows 002 dark-field (DF) TEM micrographs of (110) and $(\bar{1}10)$ cross sections of a $(GaAs)_{0.78}(Ge_2)_{0.22}$ layer, grown at 675˚C at Spire, which exhibits pronounced phase separation. This layer was grown on a (001) GaAs substrate, miscut 2˚ toward (010), at a rate of ≈ 2.4 μm per hour. The substrate was rotated at ≈ 15 revolutions per minute during growth. In this picture, the Ge-rich regions appear dark because the 002 reflection is forbidden for the diamond cubic structure of Ge. In the (110) cross section, the Ge-rich regions in the layer form an interconnected network of ribbons forming a cell-like structure embedded in GaAs-rich zinc-blende material. The Ge-rich regions are not antiphase boundaries in these layers, and so are different from the Ge-mediated antiphase boundaries previously reported in sputter-deposited layers (Romano et al 1987). Thicker Ge-rich plates, oriented close to (001), occur in some areas, and are connected by Ge-rich ribbons having a tendency to lie on {115}B planes. These {115}B Ge-rich ribbons in many cases are not continuous and show spot-like contrast, indicating that they are composed of closely spaced clusters or rods of Ge-rich material. In the orthogonal $(\bar{1}10)$ cross section, Fig. 1(b), the Ge-rich regions show a completely different morphology, and form a series of dark contrast bands, ≈5-10 nm thick, inclined by ≈2˚ to the $(GaAs)_{1-x}(Ge_2)_x$ layer/GaAs buffer layer interface. This inclination we believe is associated with the offcut of the substrate from (001). The bands are not continuous and gradually appear and disappear as you move along them. A low density of small antiphase domains was observed in some regions associated with the growth of zinc-blende GaAs-rich material on thick, Ge-rich, diamond cubic plates. No extra diffraction spots were observed in transmission electron diffraction (TED) patterns, which rules out the existence of GeAs or $GeAs_2$ phases because their crystal structures are different from GaAs and Ge (Pearson 1967). A $(GaAs)_{0.78}(Ge_2)_{0.22}$ layer, grown at the National Renewable Energy Laboratory (NREL), at 640˚C without substrate rotation, on an (001) GaAs substrate offcut 2˚ toward $(\bar{1}10)$, showed a similar phase-separated microstructure (Norman et al 1999), indicating that substrate rotation was not responsible for the phase-separated microstructure in the sample of Fig. 1.

Fig. 1. 002 DF TEM micrographs of $(GaAs)_{0.78}(Ge_2)_{0.22}$ layer, grown at Spire at 675˚C, showing pronounced phase separation: (a) (110) cross section; (b) $(\bar{1}10)$ cross section.

Fig. 2 shows (110) cross-section, 002 DF micrographs of $(GaAs)_{0.90}(Ge_2)_{0.10}$ layers grown at NREL at 643˚, 666˚, and 689˚C, separated by thin InGaP spacer layers, on a (001) GaAs substrate offcut 2˚ toward $(\bar{1}10)$. In the layer grown at 643˚C, Fig. 2(a), the phase-separated microstructure is remarkably regular, with thin sheets of Ge-rich material lying on both sets of {115}B planes forming a diamond pattern as they intersect (Norman et al 1999). The Ge-rich sheets are not continuous in some areas and are formed of closely spaced clusters or rods of Ge-rich material lying on the {115}B planes. AFM of the growth surface of a similar $(GaAs)_{0.90}(Ge_2)_{0.10}$ layer, Fig. 3, clearly shows {115}B surface facets, which are identical to the planes observed for the Ge segregation in this sample (Norman et al 1999), suggesting that the Ge segregation and the growth surface morphology are related. In the layer grown at 666˚C, Fig. 2(b), it can be seen that thicker, (001)-oriented, Ge-rich plates are starting to form and are connected by thin Ge-rich sheets on {115}B planes. Antiphase domains, e.g., marked APD in Fig. 2 (b), are sometimes formed in this layer during overgrowth of the Ge-rich, diamond cubic plates by the zinc-blende GaAs-rich material. In the layer grown at 689˚C, Fig. 2(c), only thick, irregular cross-section, (001)-oriented plates of Ge-rich material are present. Convergent beam electron diffraction indicates that the Ge-rich plates have the diamond cubic structure, whilst the GaAs-rich material is zinc-blende. In the orthogonal $(\bar{1}10)$ cross section, the Ge-rich regions again appeared as discontinuous bands, inclined at a slight angle to (001), whose thickness and length increased with growth temperature. As far as we know, the only previous report of similar phase-separated microstructures in a semiconductor alloy was that of Seong et al (1993) for MBE $InAs_ySb_{1-y}$ alloys grown at low temperatures. Growth of a $(GaAs)_{0.90}(Ge_2)_{0.10}$ layer at 640˚C, on a {115}B GaAs substrate, resulted in the phase separation only occurring on the {115}B planes parallel to the growth surface, Fig. 4, forming a "natural" GaAs/Ge superlattice along the growth direction.

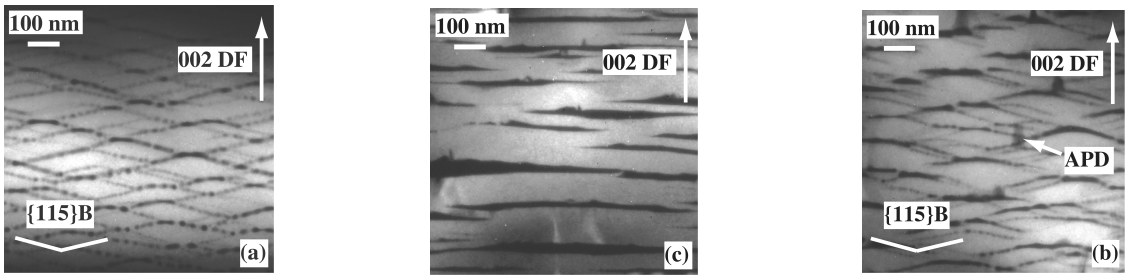

Fig. 2. (110) cross-section, 002 DF TEM images showing phase-separated microstructure of $(GaAs)_{0.90}(Ge_2)_{0.10}$ layers, grown at NREL at: (a) 643˚C; (b) 666˚C; and (c) 689˚C

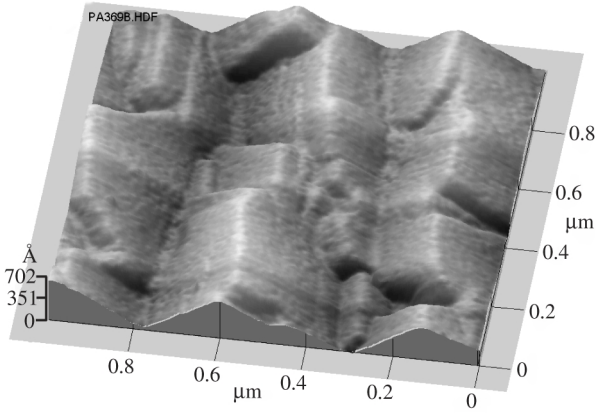

Fig. 3. AFM image of growth surface of $(GaAs)_{0.90}(Ge_2)_{0.10}$ layer, grown at 640˚C, showing {115}B surface facets.

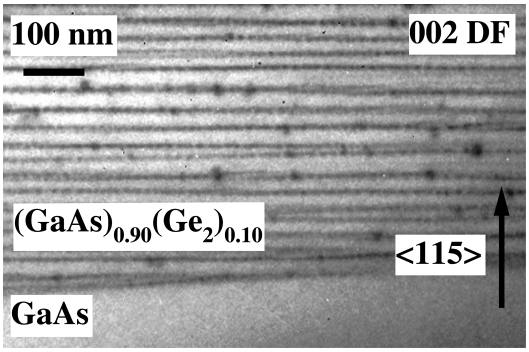

Fig. 4. (110) cross-section, 002 DF, TEM image of {115}B $(GaAs)_{0.90}(Ge_2)_{0.10}$ layer grown at 640˚C containing "natural" superlattice along [115]B growth direction.

4. DISCUSSION AND CONCLUSIONS

The characteristic phase-separated microstructure found in the $(GaAs)_{0.90}(Ge_2)_{0.10}$ layers grown at 640˚C, we suggest, may develop as follows. As the $(GaAs)_{0.90}(Ge_2)_{0.10}$ layer starts growing, the GaAs-rich phase deposits first, with the excess Ge segregating to the growing layer surface because the formation of the high-energy As-Ge and Ga-Ge bonds is unfavourable. The accumulation of excess Ge at the surface triggers the spontaneous formation of {115}B surface facets to lower the surface energy. After the surface Ge concentration reaches a critical value, nucleation of Ge-rich material occurs on the {115}B facets. The excess surface Ge then precipitates out, conformal to the growth surface, because it can now form low-energy Ge-Ge bonds at the edges of the Ge-rich nuclei. The GaAs-rich phase continues to grow and repetition of the above growth behaviour results in the observed microstructure. The repeated surface segregation of Ge, followed by nucleation and growth of Ge-rich material once a critical surface Ge concentration is reached, could explain the quasi-periodic nature of the GaAs/Ge "natural" superlattice along the growth direction of sample grown on a {115}B substrate, Fig. 4. The growth process is really a simple eutectic solidification, but from the vapour phase rather than from the more normal liquid phase. A low density of antiphase domains is observed in the GaAs-rich phase, despite the growth of the polar, zinc-blende GaAs-rich material on top of the non-polar diamond cubic Ge-rich material. This may be a consequence of epitaxial lateral overgrowth of the Ge-rich phase by GaAs-rich material emanating from holes in the Ge rich sheets or gaps between Ge-rich plates. The polarity of this GaAs-rich material is determined by the underlying GaAs-rich phase, thus reducing the formation of antiphase domains. Photoluminescence measurements on a series of phase-separated $(GaAs)_{1-x}(Ge_2)_x$ layers, grown across the composition range, by Spire (Vernon et al 1994) revealed pronounced band-gap narrowing which we believe may be a consequence of the phase separation.

In conclusion, we have observed pronounced phase separation in $(GaAs)_{1-x}(Ge_2)_x$ alloy layers, grown by low-pressure MOVPE, that may cause substantial band-gap narrowing in these samples. The phase-separated microstructure depended on alloy composition, growth temperature, and substrate orientation.

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